Nebraska, discovered by James H. Cook in 1897. After the lapse of the Carnegie researches and explorations, the American Museum entered this quarry and through five years of continuous exploration (1911-1916) an irregular area within a square of about 36 feet yielded nearly complete skulls of ten individuals and skeletal parts of seventeen individuals all-together. From this wonderful material it has been possible to supplement the descriptions of Holland and Peterson and to present for the first time the proportions and pose, by which we may estimate the habits of this animal. We reach the conclusion that the Moropus type was not plains living, but forest living; that it was the seclusion of the forests which protected this type and which accounts for its great rarity in fossil deposits, for it is characteristic of forestliving forms that they are not readily entombed. We form an entirely different conception of the habits of the animal when we observe the extremely long fore limbs, which are not of the digging or fossorial type, and which thus belie the apparently fossorial or digging structure of the terminal phalanges. It appears more probable that these terminal claws were used partly for purposes of offense and defense, but largely for the pulling down of the branches of the trees. The animal was probably forest living like the African okapi, with which in its general body and head proportions it has many analogies. Like the okapi it survived through retreat to the recesses of the forests.

THE STRUCTURE OF ATOMS AND THE OCTET THEORY OF VALENCE

By IRVING LANGMUIR

RESEARCH LABORATORY, GENERAL ELECTRIC COMPANY, SCHENECTADY, NEW YORK

Read before the Academy, April 29, 1919

In a paper soon to be published in the Journal of the American Chemical Society, I will give a new theory of the structure of atoms and molecules based upon chemical data. This theory, which assumes an atom of the Rutherford type, and is essentially an extension of Lewis' theory of the 'cubical atom,' may be most concisely stated in terms of the following postulates.

- 1. The electrons in atoms are either stationary or rotate, revolve or oscillate about definite positions in the atom. The electrons in the most stable atoms, namely, those of the inert gases, have positions symmetrical with respect to a plane called the equatorial plane, passing through the nucleus at the center of the atom. No electrons lie in the equatorial plane. There is an axis of symmetry (polar axis) perpendicular to the equatorial plane through which four secondary planes of symmetry pass, forming angles of 45° with each other. These atoms thus have the symmetry of a tetragonal crystal.
- 2. The electrons in any given atom are distributed through a series of concentric (nearly) spherical shells, all of equal thickness. Thus the mean

radii of the shells form an arithmetric series 1, 2, 3, 4, and the effective areas are in the ratios 1: 2²: 3²: 4².

- 3. Each shell is divided into cellular spaces or cells occupying equal areas in their respective shells and distributed over the surface of the shells according to the symmetry required by postulate 1. The first shell thus contains 2 cells, the second 8, the third 18, and the fourth 32.
- 4. Each of the cells in the first shell can contain only one electron, but each other cell can contain either one or two. All the inner shells must have their full quotas of electrons before the outside shell can contain any. No cell in the outside layer can contain two electrons until all the other cells in this layer contain at least one.
- 5. When the number of electrons in the outside layer is small, these electrons arrange themselves over the underlying ones, being acted on by magnetic attractive forces. But as the charge on the kernel or the number of electrons in the outside layer increases, the electrostatic repulsion of the underlying electrons becomes predominant and the outer electrons then tend to rearrange themselves so as to be as far as possible from the underlying ones.
- 6. The most stable arrangement of electrons is that of the pair in the helium atom. A stable pair may also be held by: (a) a single nucleus; (b) two hydrogen nuclei; (c) a hydrogen nucleus and the kernel of another atom; (d) two atomic kernels (very rare).
- 7. The next most stable arrangement of electrons is the octet; that is, a group of eight electrons like that in the second shell of the neon atom. Any atom with atomic number less than twenty, and which has more than three electrons in its outside layer tends to take up enough electrons to complete its octet.
- 8. Two octets may hold one, two, or sometimes three pairs of electrons in common. One octet may share one, two, three or four pairs of its electrons with one, two, three or four other octets. One or more pairs of electrons in an octet may be shared by the corresponding number of hydrogen nuclei. No electron can be shared by more than two octets.

The inert gases are those having atoms in which all the cells in the outside shell have equal numbers of electrons. Thus according to the first four postulates the atomic numbers of the inert gases should be 2, 10, 18, 36, 54, and 86 in agreement with fact.

All atoms with an atomic number greater than that of helium, have as their first shell a pair of electrons close to the nucleus. The line connecting the two electrons establishes the polar axis for the atom. Neon has in its second shell eight electrons, four in each hemisphere (i.e., above and below the equatorial plane), arranged symmetrically about the polar axis. The eight electrons are thus nearly at the corners of a cube. In argon there are eight more electrons in the second shell.

The eight electrons in the third shell of the atom of iron are arranged over the underlying electrons in the second shell. The two extra electrons in the atom of nickel are placed in the polar axis. Beyond nickel the electrons in the atom cannot be held by magnetic forces, and thus tend to rearrange themselves so as to be placed as far as possible from the underlying electrons. This leads to an explanation of the chemical and magnetic properties of copper, zinc, etc.

Krypton has in its third shell nine electrons in each hemisphere, symmetrically placed with respect to the polar axis and to the four electrons in the second shell. The ninth electron in each hemisphere goes into the polar axis. Xenon is like krypton, except that it has twice as many electrons in its third shell. Beyond Xenon eighteen electrons in the fourth shell can be held by magnetic forces over the eighteen cells of the third shell, so that lutecium, the eighteenth element beyond Xenon marks the last of the rare earth elements. The electrons in the outside shell of the atoms beyond this element are arranged as far as possible so as to leave eighteen empty spaces over the underlying electrons. In this way it is possible to explain the chemical and magnetic properties of tantallum and tungsten as contrasted to those of the rare earths.

Niton has sixteen electrons in each hemisphere of its fourth shell. These are placed symmetrically with respect to the polar axis and the eight underlying electrons.

This theory of atomic structure explains in a satisfactory way most of the periodic properties of all the elements including those of the eighth group and the rare earths. It lends itself especially well to the explanation of the so-called physical properties, such as boiling-points, freezing-points, electric conductivity, etc. For the details of its application to specific elements the paper in the *Journal of the American Chemical Society* should be consulted.

Postulates 6, 7 and 8 lead directly to a new theory of valence which we may call the Octet Theory. This theory may be stated in terms of the equation

$$e = 8n - 2p \tag{1}$$

where e is the total number of available electrons in the shells of all the atoms in a molecule; n is the number of octets forming the outside shells of the atoms and p is the number of pairs of electrons held in common by the octets (Postulate 8). If we let E be the number of electrons in the 'shell' of an atom then $e = \sum (E)$. The value of E for a given atom, at least in case of the first twenty elements, corresponds to the ordinal number of its group in the periodic table. Thus we have the following values of E:—one for hydrogen, lithium, sodium, etc., two for magnesium, three for boron, aluminum, etc.; four for carbon and silicon, five for nitrogen and phosphorus; six for oxygen and sulphur; seven for the halogens, and zero for the inert gases.

The above equation expresses the fact that every pair of electrons held in common between two octets results in a decrease in two in the total number of electrons needed to form the shells of the atoms in the molecules. It also implicitly expresses the fact that *all the electrons* in the shells of the atoms forming a molecule form part of one or two of the octets in the molecule.

It seems that this simple equation is a practically complete statement of a theory of valence that applies with very few exceptions to all compounds formed from the first twenty elements. With some modifications it applies also to most compounds of other elements. In the case of organic compounds it is found that each pair of electrons held in common between atoms corresponds exactly to the valence bond used in the ordinary theory of valence. It is therefore proposed to define valence as the number of pairs of electrons which a given atom shares with others. In view of the fact known that valence is very often used to express something quite different, it is recommended that the word covalence be used to denote valence defined as above.

Equation (1) expresses the fact that the number of covalence bonds in a molecule must be related to the number of available electrons in the molecule. A simple mathematical analysis² shows that all structural formulas written according to the ordinary valence theory in which the valence for each element is taken equal to 8–E, will satisfy Equation (1). Thus the Octet Theory requires no modification in any formula written with the following valencies; carbon-four, nitrogen-three; oxygen-two; chlorine-one and hydrogen-one. In some cases, however, the Octet Theory suggests that other formulas besides those usually adopted may be possible. Whenever the old theory of valence has assumed valencies other than those mentioned above, such as five for nitrogen or phosphorus; four or six for sulphur; three, five or seven for chlorine, etc., the Octet Theory gives quite different structural formulas from those usually assumed. This is readily seen when it is considered that the covalency of an element according to the Octet Theory can never exceed four, since there are only four pairs of electrons in an octet.

A careful examination of the cases showing a discrepancy between the old and new theories furnishes the strongest kind of evidence in support of the Octet Theory. The non-existence of such compounds as H₄S, H₆S, SCl₆, NCl₅, NH₆, etc., is in full accord with the theory as is also the existence of SO₂, SO₈, N₂O₅, HNO₃, NH₄Cl, etc. In these latter cases, however, the formulas written are different from those usually adopted. For example, the covalence of sulphur is three in SO₂, four in SO₃; that of nitrogen is four in N₂O₅, HNO₃, and NH₄Cl. These covalencies are, however, not assumed as in the ordinary valence theory, but are derived from Equation (1), which is the same equation as that which applies to all ordinary organic compounds. In a similar way it is found that the Octet Theory fully explains the structures of such compounds as N₂O, N₂O₃, N₂O₄, HN₃, N(CH₃)₄Cl, H₃PO₃, H₃PO₄, HClO, HClO₂, HClO₃, HClO₄, H₂O₂, and even so-called complex compounds such as B(CH₃)₃, NH₃, K₂PtCl₂.2NH₃, KBF₄, Na₂S₅, etc.

From this viewpoint a very large number of compounds previously considered by Werner are found to be typical primary valence compounds not essentially different in their structures from organic compounds. It is especially significant that the structure of these compounds is found from Equation (1), without any additional assumptions. Thus we are lead to a *single theory* of

valence which explains and coördinates the separate valence theories that we have needed in the past.

There are many facts not previously well understood which are very readily explained by the new theory. For example, the fact that we have weak and strong acids, weak and strong bases, but no 'weak' and 'strong' salts, is automatically explained.

The theory indicates that all salts consist of negative and positive ions even when in the solid condition, and that no pair of electrons are held in common between the negative and positive groups. Thus in sodium chloride the covalence of both sodium and chlorine is zero, and this fact explains the non-existence of molecules of sodium chloride shown by the X-ray crystal analysis. When sodium chloride is dissolved in water the water does not cause ionization, but simply causes the separation of atoms already ionized. This direct result of the Octet Theory is in full accord with experiment and with Milner's recent theory of strong electrolytes. London, Phil. Mag., 35, 1918, (214, 354).

In the field of organic compounds the theory fits the facts particularly well. Although in the case of compounds like SF₆, H₂SiF₆, etc., there is very definite evidence that the kernels of the atoms of sulphur and silicon are cubical in shape, there is the strongest evidence that in organic compounds the carbon atom has the eight electrons of its octet drawn together into four pairs, arranged at the corners of a tetrahedron. This is in full accord with the fact that in SF6, and H2SiF6, the central atom has given up electrons to the surrounding atoms, so that the cubical kernels do not share any electrons with the other atoms, while in organic compounds the carbon atoms always share four pairs of electrons with adjacent atoms. From this we must conclude that a pair of electrons held in common by two octets acts as if it were located at a point between the two atoms. This conclusion, which can be reduced from the properties of a very few simple organic compounds is found to apply apparently without exception to compounds of nitrogen, sulphur, phosphorus, and even cobalt compounds, etc. It seems to explain all the cases of stereoisomerism that I am familiar with. For example, in the amine oxides, NR₁R₂R₃O, nitrogen is quadricovalent, so that these substances exist as optical isomers, just as in the case of a carbon atom attached to form different groups.

The isomerism of compounds of tervalent nitrogen such as ketoximes, hydrazones, ozazones, and diazo-compounds, etc., is readily accounted for, as well as the absence of isomers among tertrary amines, etc. Not only are the substituted ammonium compounds fully explained, but also the sulfonium, phosphonium, and oxonium compounds. Thus the structures of S(CH₃)₄OH, S(CH₂)₄Cl₂, (C₂H₅)₂O.HCl, etc., are readily found from the Octet Theory and their salt-like character is explained. The covalence of the central atom in the above compounds is three, four and three respectively.

When the values of e and n are both the same for two or more compounds it is evident according to the Octet Theory that these may have practically identical structures. An example of this kind is found in N_2 and CO. The total

number of electrons in each molecule (including those in their kernels) is fourteen. Evidence is given in the paper in the *Journal of the American Chemical Society* that the structures of these two molecules is identical, except for the fact that in one case there are two nuclei of seven positive charges each, while in the other there are nuclei of six and eight charges, respectively. These molecules are, however, exceptional, in that the molecule consists of a *single* octet arranged around a complex kernel.

Another example of a pair of compounds which according to the Octet Theory should have similar structures occurs in the case of CO_2 and N_2O . For each of these molecules n=3, e=16 and therefore p=4. The best method of testing this conclusion lies in comparing the 'physical' properties of the two substances. The 'chemical' properties depend primarily on the ease with which the molecules can be broken up, and thus is a measure of the internal forces within the molecule, which depend to a large extent on the charges on the kernels. The so-called 'physical' properties on the other hand depend on the stray field of force outside of the molecule, and this naturally depends rather on the arrangement of the outside electrons.

As a matter of fact we find that most of the physical properties of these two gases are practically identical.

The following data taken from Landolt-Börnstein tables and Abegg's hand book illustrate this.

	N ₂ O	CO2
Critical pressures	75	77 atmos.
Critical temperatures	35.4°	31.9°
Viscosity at 20°C	148 × 10 ⁻⁶	148 × 10 ⁻⁴
Heat Conductivity at 100°C	0.0506	0.0506
Density of Liquid at -20°	0.996	1.031
Density of Liquid at +10°	0.856	0.858
Refractive index of liquid. D line, 16°C	1.193	1.190
Dielectric constant of liquid at 0°	1.598	1.582
Magnetic susceptibility of gas at 40 atmos. 16°C	0.12 × 10 ⁻⁶	0.12×10^{-6}
Solubility in water 0°	1.305	1.780
Solubility in alcohol at 15°	3.25	3.13

Both gases form hydrates $N_2O.6H_2O$ and $CO_2.6H_2O$. The vapor pressure of the hydrate of N_2O is 5 atmospheres at $-6^{\circ}C$, while the hydrate of CO_2 has this vapor pressure at $-9^{\circ}C$. The heats of formation of the two hydrates are given respectively as 14,900 and 15,000 calories per gram molecule.

The surface tension of liquid N₂O is 2.9 dynes per cm. at 12.°2, while CO₂ has this same surface tension at 9.0°.

Thus N₂O at any given temperature has properties practically identical with those of CO₂ at a temperature 3° lower.

These results establish the similarity of outside structure of the molecules.

There is one property however, which is in marked contrast to those given above. The freezing-point of N_2O is -102° while that of CO_2 is -56° . This fact may be taken as an indication that the freezing-point is a property which is abnormally sensitive to even slight differences in structure. The evidences seem to indicate that the molecule of CO_2 is slightly more symmetrical, and has a slightly weaker external field of force than that of N_2O . Such differences could easily be produced by the difference in the charges on the kernels.

There are many other examples of compounds having similarly formed molecules. It will be convenient to call these *isosteric compounds* or *isosteres*. These may be defined as compounds whose molecules have the same number and arrangement of electrons.

Another example of a pair of isosteres is that of HN₃ and HCNO. The similarity of properties should be most marked in the salts of these acids. The available data on solubilities and crystalline form seem to show that the salts of these two acids are very closely similar in physical properties.

This relationship of compounds may be carried much further. Thus, according to the Octet Theory, we should regard CH₄ as an isostere of the NH₄ ion. The electric charge on the ion prevents a direct comparison of physical properties. Other examples are:

The carbonate and nitrate ions:

$$O \cap C = O \text{ and } O \cap N = O$$

The orthophosphate, sulphate and perchlorate ions:

Sulfur trioxide and the metaphosphate ion:

$$O S = O$$
 and $O P = O$

The hydrofluoric acid molecule and the hydroxyl ion:

$$H - F$$
 and $O - H$

The sulfite and the chlorate ions:

We may attribute the differences in physical properties in all these cases to the effect of the differences in the electric charges.

Lewis has already pointed out that a theory of the kind outlined in this paper explains satisfactorily the facts which have led many chemists to assume polar valence. For example, the chlorine atom in chlor-acetic acid, because of the relatively large charge on its kernel, as compared for example with a carbon atom, tends to displace towards itself the electrons holding it to the carbon atom. This effect is transmitted with gradually decreasing intensity to the further end of the molecule, where it results in drawing the pair of electrons which holds the hydrogen nucleus to the octet of the oxygen atom, away from the hydrogen nucleus. Another way of looking at the effect is to consider that the positive kernel of the oxygen atom is displaced toward the hydrogen nucleus, and thus tends to weaken the force holding it. This effect makes it easier for the hydrogen nucleus to separate from the rest of the molecule as a positive ion. It is felt that this explanation can be applied in general to explain nearly all cases where polar valence bonds have been assumed in the past. This question will be discussed in more detail in the second paper to be published in the Journal of the American Chemical Society.

'A NEW INSTRUMENT FOR MEASURING PRESSURES IN A GUN

By A. G. Webster and L. T. E. Thompson

BALLISTIC INSTITUTE, CLARK UNIVERSITY, WORCESTER, MASSACHUSETTS*

Read before the Academy, April 29, 1919

It is now over fifty years since the crusher gauge was invented for measuring the maximum pressure developed in a gun. This apparatus has probably gone through fewer changes than almost any physical instrument except the telegraphic sounder. It is looked upon by all experts as inaccurate, and should be superseded. We have developed an apparatus which shows not only maximum pressure, but also the pressure at any time while the projectile is in the barrel; that is, it gives the curve which represents the pressure as a function of the time. Attention is called to the fact that this curve is not obtained by a series of points, and that no part of the curve is missing. The success of this instrument is due to its being designed in accordance with the principles of dynamics, and of optics.

The general nature of the apparatus is shown in figures 1 and 2. The success of such an apparatus that is to be free from vibrations of its own is brought about by using an extremely stiff spring. Such a spring is obtained by a short, steel girder, or a circular plate, the girder being shown in

¹ Lewis, G. N., J. Amer. Chem. Soc., 38, 1916, (762-785).

² This will be published in full in a paper soon to be submitted to the *Journal of the American Chemical Society*. This second paper will deal in some detail with the application of the Octet Theory to organic chemistry, particularly to nitrogen, sulphur, compounds, etc. The stereoisomerism of such compounds will be discussed.

^{*} Contribution from the Ballistic Institute, Clark University No. 4.